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SOME PHYSICAL PROPERTIES OF LIQUIDS IN A TWO-LAYER HYDRODYNAMIC--ETC(U)
JAN 64 J R OLSON, A A HUDIMAC

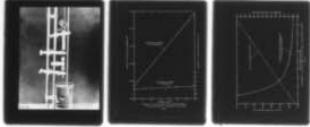
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SOME PHYSICAL PROPERTIES OF LIQUIDS IN A TWO-LAYER HYDRODYNAMIC MODEL.

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PREFACE

This memorandum is not to be construed as a report since its only function is to present a small portion of the work performed as part of NEL Problem L4-4 in basic Navy Operations Research.

The memorandum has been prepared in this form because it is believed that this information may be useful to others at NEL and to a few persons or activities outside NEL.

Acknowledgment of assistance given by R. B. Nebrich Jr. in selecting and procuring liquid samples is gratefully made.

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SOME PHYSICAL PROPERTIES OF LIQUIDS IN A
TWO-LAYER HYDRODYNAMIC MODEL

by

J. R. Olson and A. A. Hudimac

U. S. Navy Electronics Laboratory

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INTRODUCTION

In the study of internal waves and associated phenomena, three methods of attack have been considered: theoretical analysis, model studies, and field experiments. The purpose of this memorandum is to discuss the results of some studies of the properties of liquids with regard to their use in model studies. This technical memorandum is intended for use at NEL and by a few persons outside the Laboratory.

The two principal types of model studies made or planned are:

(a) a study of the internal wave system in a two-layer liquid model, due to a moving body, (b) the determination of the internal wave-making drag of a body moving in a two-layer liquid system. In both of these cases, dimensional analysis has been used to show that the experimental results can be scaled if two dimensionless parameters, (among others), $\Delta\rho/\rho^1$, and $F^2 = c^2\rho^1 / \Delta\rho gh$, are kept constant. Here, the pertinent liquid properties that must be known are ρ^1 , the density of the lower liquid layer, and $\Delta\rho$, the difference between densities of the two liquid layers. F = Froude number, c = source (or body) velocity, g = acceleration due to gravity, h = upper layer thickness.

Thus one of the principle properties of the liquids used in the model studies is the density of the liquids. The difference in density appears explicitly, and this difference must be quite small (~ 0.001 gm/cm³). Hence the densities must be measured very accurately, or else a method that determines the difference in densities

with adequate accuracy (~5%) had to be developed; the latter was done.

In scaling an experiment, care must be taken that nothing peculiar to the model system is contrary to the hydrodynamic behaviour existing in the large scale. One such peculiarity is the property of interfacial surface tension. The effect of this property on the velocity of propagation of internal waves has been studied (see reference 1). It was decided that interfacial surface tensions of greater than 1 dyne/cm could not be tolerated. Detergents were used to suppress interfacial surface tension. Methods were developed to determine the amount of suppression.

In addition to the above fluid characteristics, there are a number of other fluid properties which had to be considered in the choice of a fluid pair. Some have to do with preserving the character of the large scale hydrodynamic behavior, and some have to do with proposed methods of observation.

Viscosity should be low enough to make valid the assumption of inviscid behaviour. The difference in index of refraction is important in optical methods for the visualization of internal waves, as are clarity and color. The role of diffusion (references 2, 3) in model studies has been studied. Thus, moderate immiscibility of the liquids is desirable, although in general a concomitant of a high degree of immiscibility is a high interfacial surface tension. The

liquids had to be safe, i.e., non-toxic and non-flammable. The fluids had to be available in large quantities at a reasonable price (quantities of 500 gal. and 1500 gal. were being considered for the large model tank).

APPARATUS

Measurement of Δp , p_0 and p

Several methods of measuring density and density difference of the fluids were considered. One such method that was tried was the use of a commercial Westphal balance. The guaranteed accuracy of the balance was not sufficient for the needs of this experiment.

This was also the case when available commercial pycnometers were tried. Both aluminum and glass types were used, however each contained relatively small volumes and trouble was encountered from evaporation and in filling the containers precisely. More refined pycnometers and procedures for using them are discussed in reference 9.

A more accurate method of determining the density of fluids (and especially the difference in density of two fluids of almost equal density) is the method of hydrostatic weighing. The method involves weighing a bob while immersed in the one and then the other of the two liquids. A thermally stable bob, whose weight in vacuum, W_v , and whose volume, V , are known is required. For accuracy, the buoyant effect of air must be taken into account.

The weight of the bob in vacuum, W_v , can be computed from

$$(1) \quad W_v = X + (V - \frac{X}{\rho_b}) \rho_a,$$

where X is the weight indicated by the weights needed to obtain balance, ρ_a is the density of air, and ρ_b is the density of the (in our case, brass) weights. To determine V , the bob should be weighed in distilled water. This corrected weight is

$$(2) \quad W_w = X_w (1 - \frac{\rho_a}{\rho_b}),$$

where X_w is the weight used. Now

$$(3) \quad V = \frac{W_v - W_w}{\rho_w} \approx W_v - W_w.$$

The volume then becomes

$$(4) \quad V = \frac{(X - X_w)(1 - \frac{\rho_a}{\rho_b})}{1 - \rho_a}$$

In the fluid whose density is ρ , the weight in the fluid is

$$(5) \quad W_\rho = X_\rho (1 - \frac{\rho_a}{\rho_b}),$$

and the density of the fluid is

$$(6) \quad \rho = \frac{W_v - W_\rho}{V}$$

Similarly, ρ' for the fluid whose density is greater than ρ may be found.

Then $\Delta\rho = \rho' - \rho$ becomes,

$$\rho' - \rho \approx \frac{W_V - W_{\rho'}}{V} = \frac{W_V - W_{\rho}}{V} = \frac{W_{\rho} - W_{\rho'}}{V}$$

or

$$(7) \quad \rho' - \rho \approx \frac{(X_{\rho} X_{\rho'})}{V} \left(1 - \frac{\rho_a}{\rho_b} \right)$$

The factor $(1 - \frac{\rho_a}{\rho_b})$ can be neglected.

The following describes a relatively easy way, which requires little apparatus, of applying the hydrostatic weighing method to measure density difference of two liquids as a function of temperature. Since the temperature range of interest included only typical room temperature variations, no effort was made in controlling the liquid temperatures. The liquid temperature was allowed to follow the room temperature and the only effort made was to accurately measure the resulting changes. Thus, these temperatures were at unequal intervals.

A glass bob from the commercial Westphal balance set was suspended by a fine wire in a glass cylinder containing the liquid under test. The weight of this bob in the fluid was measured with an analytical balance. The temperature of the liquid was taken with a glass thermometer, calibrated to $\pm 0.02^{\circ}\text{C}$, before and after the weight reading. The temperature associated with the weight of the

bob was taken as the mean of these two temperature readings. Usually, these two values were within 0.1°C. The liquid was well stirred with the thermometer and by moving the bob up and down. This process was repeated as the room temperature changed and thus a series of weight readings as a function of temperature for one liquid was found. A smooth curve was then drawn through these points. See figure 1.

This entire procedure was then repeated for the second liquid, which gave a second series of weight readings as a function of temperature. A smooth curve was also fitted through these points. See figure 2.

Equation 7 was then used to calculate the density difference between the two liquids. The interpolated values from the curves in figures 1 and 2 were used in this equation, because for a particular calculation of density difference, the values of X_p and X_w have to correspond to the same temperature. These calculated values of density difference were then plotted in figure 3 as a function of temperature and a smooth curve fitted through them.

In the work described in the previous section, it was awkward to depend on the room temperature changes. It was more desirable to have temperature control. Therefore, at a prescribed temperature, changes in density difference due to different additives (for interfacial tension reduction) and different concentrations of the same additive to the water phase could be determined. To accomplish

this, a cylindrical, constant temperature bath assembly which could actually be placed within the balance case was employed. See figure 4. This assembly, supported by a ring stand, is carefully placed within the balance so as not to touch the balance pan or its supports. The constant temperature water for this bath assembly was supplied from a commercial thermostat controlled source with built in circulating pump.

The bath assembly details are shown in figure 5. The assembly, constructed from copper, consists of a removable inner cylinder, F, placed in a double walled outer cylinder, D. These two cylinders are separated by a water jacket, E. The double walled cylinder, D, carries the moving water from the thermostat controlled source after passing through the inlet tube, B, down and around a helical shaped baffle and then to the outlet tube, C. Thermal insulation is provided by rubber tubing, J, by cork, G, and by a removable Plexiglas top, A. The cube, I, is suspended by support wire, K, into the liquid, H, under test.

Two cubes were made for this bath assembly. The first cube was made from fused quartz. Quartz was used as a material because of its very low coefficient of thermal expansion ($\alpha \ll 0.54 \times 10^{-6} / ^\circ\text{C.}$). This cube which had a volume of approximately 8 cubic centimeters was supported by a 0.004 inch stainless steel wire. A small wire hook was glued to the quartz cube with

Armstrong A-12 epoxy cement. The second cube that was used was made from aluminum and was approximately 33 cubic centimeters in volume. This cube was painted with "Laminar x-500" polyurethane paint for protection from the liquids to be tested.

The following procedure was used to find density difference. The liquid under test was allowed to come to equilibrium at the desired temperature while being stirred. The Plexiglas top was put in place and then the assembly was placed inside the balance case. The balance was zeroed and the support wire connected. The weight of the cube was then found, the support wire disconnected, and the balance zero rechecked. After removing the assembly from the balance case, the temperature of the liquid was rechecked. This procedure was usually repeated two more times and the mean weight was used for calculations. The weight of the cube in air, using the same support wire, was then found. After finding the mean weight of the cube in the second liquid at the same temperature, the density difference was calculated using formula 7.

Interfacial Tension Measurement

There are many methods available for the measurement of surface and interfacial tension. See references 4, 5, and 6. Static values can be obtained by the ring method (Du Nouy tensiometer), drop weight method, capillary height method, pendent drop method, ripple method, Seaside drops, film balances (vertical and horizontal).

and the maximum bubble pressure method. The first five of these can be used for interfacial tensions as well as for surface tensions. Dynamic values can be obtained by the oscillating jet and oscillating drop methods.

Both the ring and the capillary height methods were tried for measuring interfacial tensions. However, both of these methods produced serious difficulties. These problems will not be discussed here.

The drop weight method(4,5,6) ..as used most often for interfacial tension measurement. This method is relatively easy and quick to use and is capable of good accuracy. The procedure consists of forming a drop of the more dense liquid into the less dense phase from the tip of a glass tube. See figure 6a. The drop is formed slowly and will finally detach itself from the tip and fall to the bottom of the container (see figure 6b). Knowing the volume of the drop, the density difference between phases, and certain constants, the interfacial tension may be determined. The buret tube shown in figures 6a and 6b holds the more dense liquid and also provides an easy way of measuring the volume of the drop. The instant when the drop tears away from the tip provides a repeatable point to take buret readings. A mean of several drops is taken if each drop volume is small. The drops must be formed at a very slow rate. Usually a formation time of 5 to 10 minutes is slow enough. In

practice, a faster rate may be used in the initial stages of formation. If the rate is too large at the instant when the drop falls, the resulting drop will be too large. Both the buret stopcock and a fine metering valve are used to obtain the proper flow rate. Vibration and liquid stirring must be kept to a minimum during the last stages of drop formation. In order to provide a constant temperature, the same bath assembly which was discussed earlier, was also used here.

The tip must be carefully made. In this case, glass was used as a material because of its wetting characteristics with respect to the two liquid phases. As shown in figure 6a, the drop wets the bottom of the tip and thus forms from the outside diameter. A good right angle edge at the tip was ground with the aid of a drill press and emory cloth. After grinding the bottom and sides of the tip smooth, the outside diameter at the end of the tip must be measured very accurately, because the value of the radius must be cubed in the calculations. This measurement can best be achieved by using a traveling microscope or a micrometer eyepiece attachment and microscope. The volume of a single drop, V , divided by this value of the radius cubed, r^3 , enables one to find a proper correction factor, f . These values of f , ranging from 0.17 to 0.27, are empirically determined to correct the drop volume and are tabulated in reference 6 as a function of V/r^3 .

Thus, the interfacial tension is calculated from the following formula:

$$(8) \quad \Gamma = \frac{Vgf(\rho' - \rho)}{r}$$

where Γ = Interfacial tension (dynes/cm),

V = Volume of drop (cm^3),

ρ' = ρ = Density difference between liquids obtained from hydrostatic weighing method (gms/cm^3),

g = Acceleration due to gravity (cm/sec^2),

r = Radius of tip (cm),

f = Correction factor, given as a function of $\frac{V}{r^3}$.

Results and Errors

Many results have been obtained with liquids such as benzene, several plasticizers and insulating oil. Additives to the water phase have included wetting agents such as Naconnol NR, Aerosol OT, sodium hydroxide, Unox, Firewater, and Alconox. A few typical results are shown in Table I. Here the top and bottom liquids are shown, along with the temperature and the resulting density difference and interfacial tension. Some of the results that can be plotted are shown in figures 3, 7, and 8. In both figures 3 and 7 the density difference as a function of temperature is shown while in figure 7, the interfacial tension is also plotted as a function of

temperature. In figure 8, both the density difference and the interfacial tension are plotted vs. the % of solute added to the water phase at 25°C.

Water at two temperatures was used to check the hydrostatic weighing method. The difference in density of the water at the two temperatures can be found from tables (reference 10) and compared with the experimental result. A five degree centigrade change produces a change in density of approximately one part per thousand. This procedure was tried twice with the following results.

Trial	Measured $\Delta\rho$ (gm/cm ³)	$\Delta\rho$ From Tables (gm/cm ³)	% Error
1	0.00128	0.00124	3.3
2	0.00108	0.00116	6.8

These errors probably resulted from temperature instability, bubbles forming on the cube and support wire, and liquid clinging to the wire. Errors due to a change in buoyancy of the 0.004 inch support wire are below the readability of the balance (0.05 mg) if the wire is submerged to the same level within \pm 2 mm.

Each liquid will exert a downward force on the support wire due to its surface tension. If the difference in surface tension between the two liquids (each measured against air) is less than

one dyne per cm., the resulting errors will be less than the readability of the balance.

Errors in the drop weight interfacial tension method were mainly due to the volume measurement of the drops. For the smaller drops, a micro syringe could be used to give more accurate volume readings. The apparatus was checked by finding the surface tension of distilled water against air. A 0.3% error resulted as compared with accepted standard values. The estimated probable error in the interfacial tension measurements of figure 7 is \pm 3%.

Discussion

The change in density difference between the two liquids with respect to temperature can be relatively large. For example, in figure 7, the slope of the straight line drawn through the points is 0.00060 gm per cm^3 per $^{\circ}\text{C}$. This agrees well with a calculated value of 0.00061 gms per cm^3 per $^{\circ}\text{C}$ based on the coefficients of thermal expansion of the plasticizer (given by manufacturer) and of pure water (the coefficient of expansion of the Alconox solution was assumed to be the same as for pure water).

This means, in practice, that if small initial values of density difference are desired in the model tanks, it may be necessary to provide some room temperature control. If the temperature was lowered, the density difference would also go down and could actually reach zero, causing instability and possible

overturning of the layers. With the low interfacial tension involved, emulsification would probably take place.

This would not be the only cause for emulsions in such two layer systems. As discussed in reference 6, "spontaneous emulsification" can occur. This is not due to any external agitation. As one case was described in the above reference, "... if the oil is placed quietly on the water, the interfacial region gradually becomes cloudy due to spontaneously formed emulsion." These emulsions also quietly "stream" from the interfacial region (sometimes called "stranding"). This stranding has been observed extending downward from the Delex 1 plasticizer -> Alconox interface in one of the model tank experiments. In three or four days the Alconox layer became uniformly cloudy.

The resulting interfacial tensions were quite constant with respect to temperature as shown in figure 7.

Some revisions would be in order for future work. Better volume measurement of the small drops could easily be done by using a micro syringe.

Another method that has not been tried as yet would enable one to find both density difference and interfacial tension "simultaneously". In this method, the drop weight procedure would be used as usual except that the drop after detachment would be caught and weighed on a pan suspended in the second fluid. In this manner

the drop would serve as a "bob" and the density difference of the two liquids could be computed simply by dividing this weight of the drop (in the second fluid) by the volume of the drop.

Table I - Typical Density Difference ($\rho' - \rho$) and Interfacial Tension (Γ) Results.

1. Benzene
2. Pure water
3. GP233 Plasticizer
4. "Adipol," Di-iso-butyl Adipate Plasticizer
5. "Delex 1," Di-Butyl-Ethyl-Adipate Plasticizer
6. 1.0% by weight NaOH solution
7. 1.0% by volume "Unox" solution
8. 10% by volume "Unox" solution
9. 1.0% "Firewater" solution
10. 0.1% by weight Naconnol NR solution

Top Liquid	Bottom Liquid	Temp. (°C)	Density Difference (gms/cm ³)	Interfacial Tension (dynes/cm)
1	2	19.0	0.1181	33.6
3	2	23.8	0.0767	22.4
4	2	24.7	0.0501	20.5
5	2	23.0	0.0041	14.4
5	7	25.0	0.0064	5.0
5	8	25.0	0.0144	2.2
5	9	25.0	0.0056	5.6
5	10	21.9	0.0040	3.2

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LIST OF FIGURES

1. X_p (Weight of Bob in "Delex 1" Plasticizer) vs. Temperature.
2. X_w (Weight of Bob in 0.10% by Weight Nacconol NR Solution) vs. Temperature.
3. Density Difference Between 0.10% by Weight Nacconol NR Solution and "Delex 1" Plasticizer.
4. Density Difference Apparatus.
5. Constant Temperature Bath Assembly.
- 6a and b. Interfacial Tension Apparatus.
7. Density Difference and Interfacial Tension vs. Temperature for "Delex 1" Plasticizer and Approximately 0.77% by Weight Alconox Solution.
8. Density Difference and Interfacial Tension vs. % Alconox by Weight for "Delex 1" Plasticizer and Alconox Solutions.

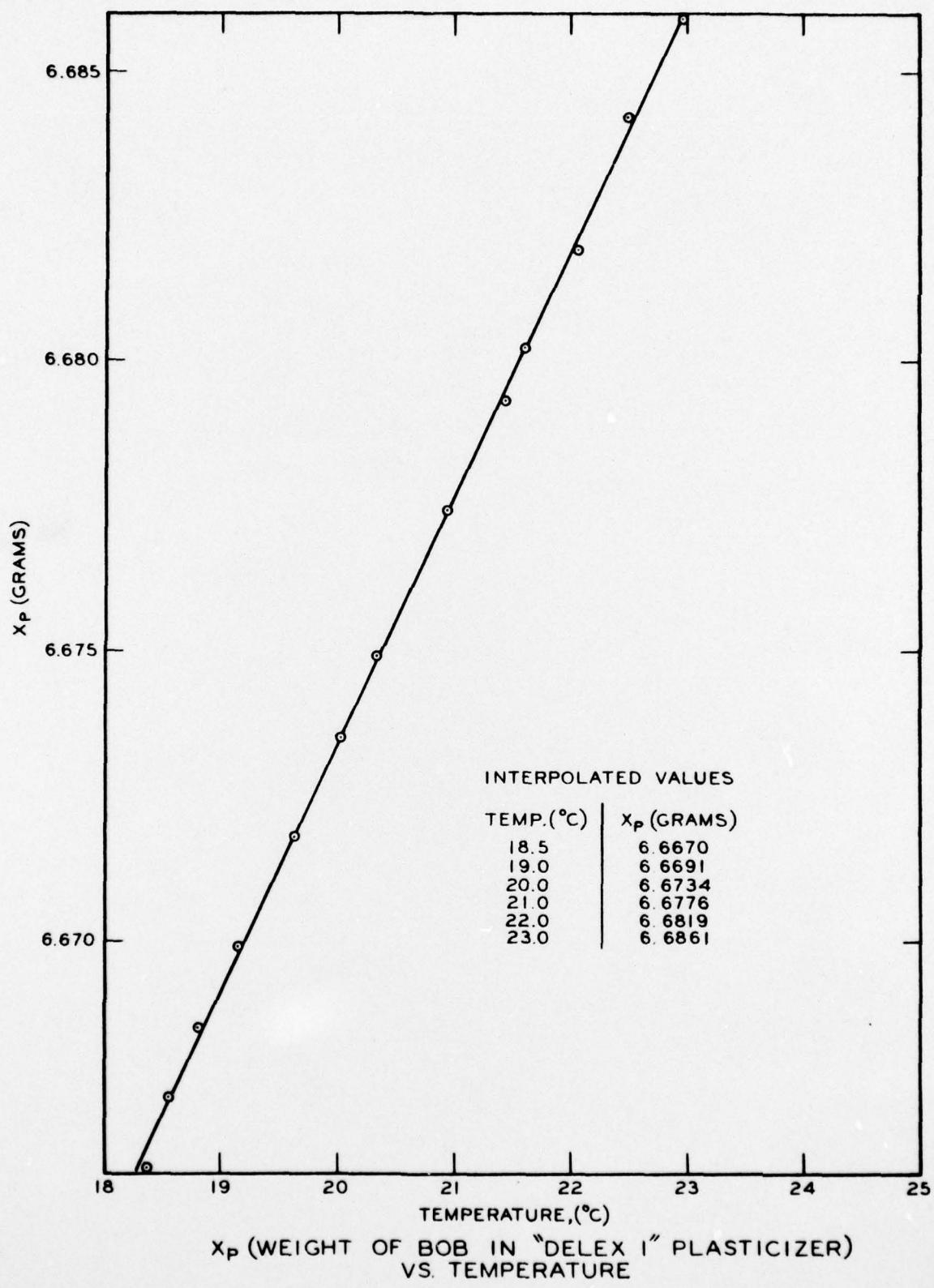


FIG. I

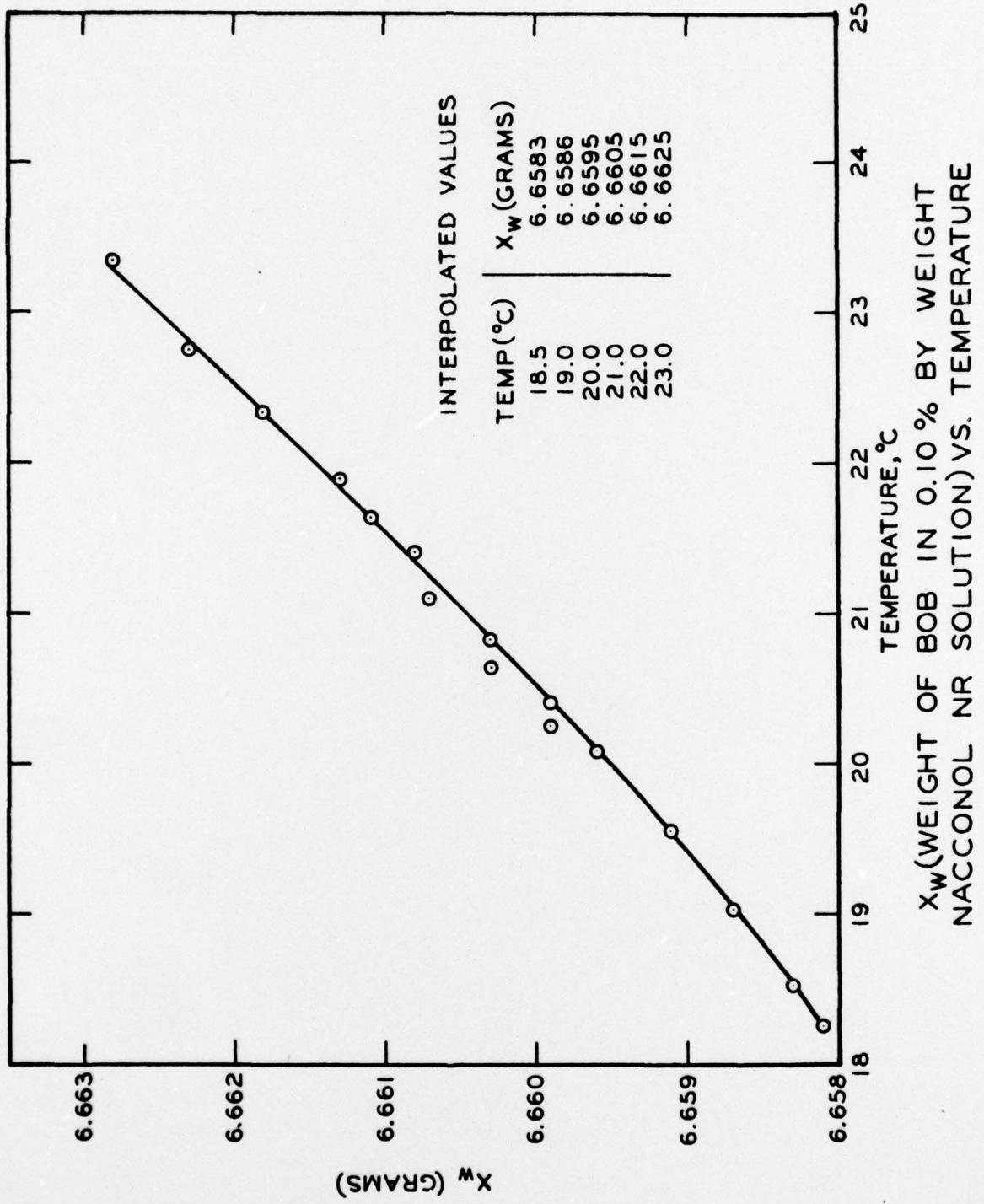
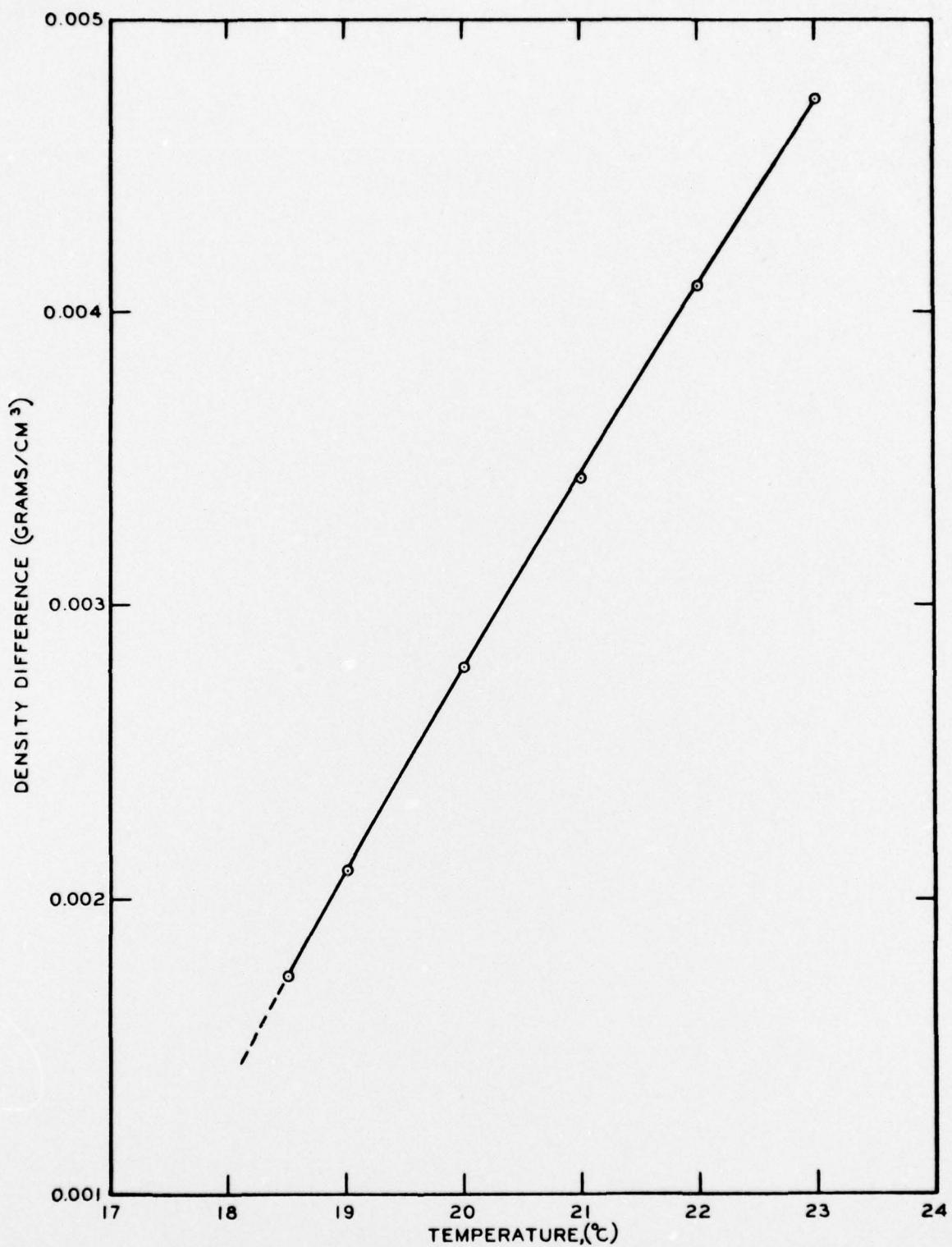


FIG. 2



DENSITY DIFFERENCE BETWEEN 0.10 % BY WEIGHT
NACCONOL NR SOLUTION AND "DELEX I" PLASTICIZER

FIG. 3

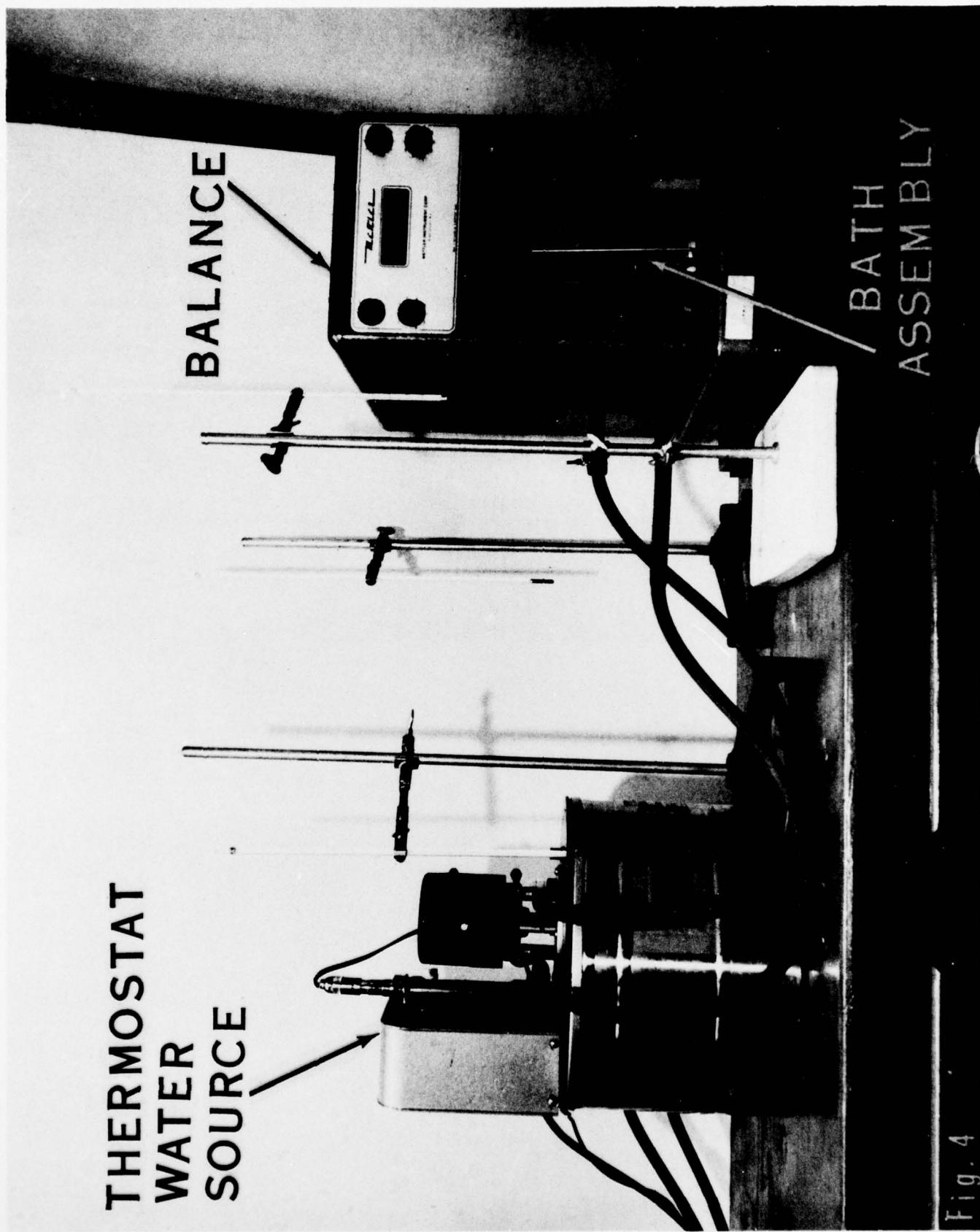
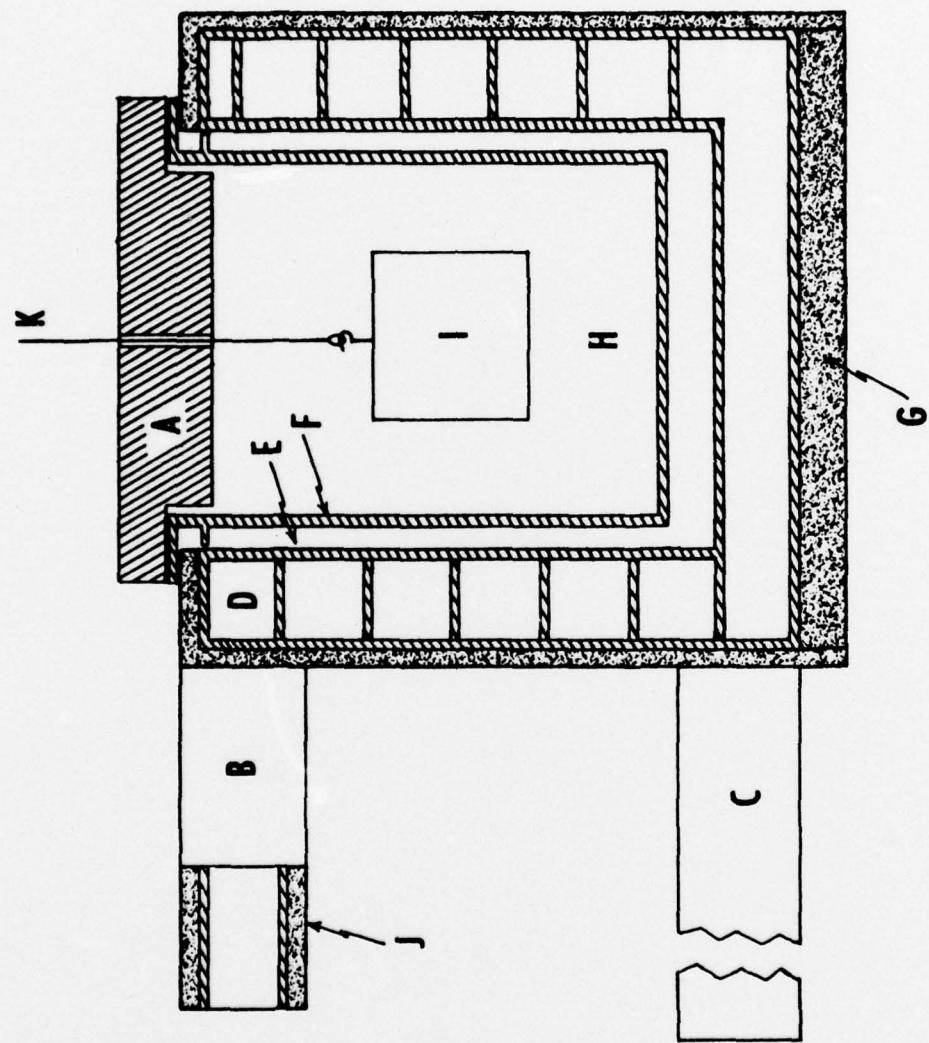


Fig. 4



CONSTANT TEMPERATURE BATH ASSEMBLY (FULL SCALE)
FIG. 5

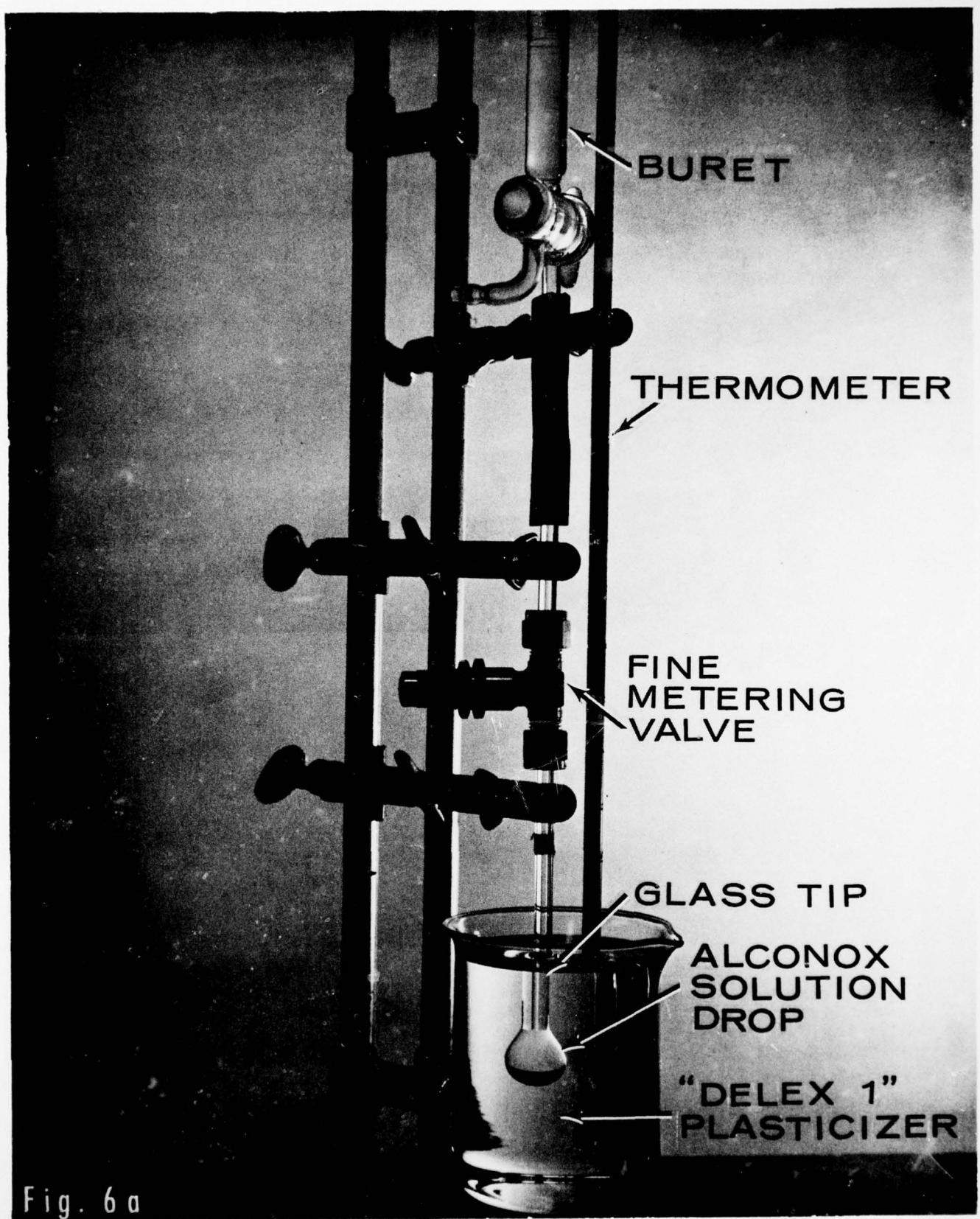


Fig. 6a

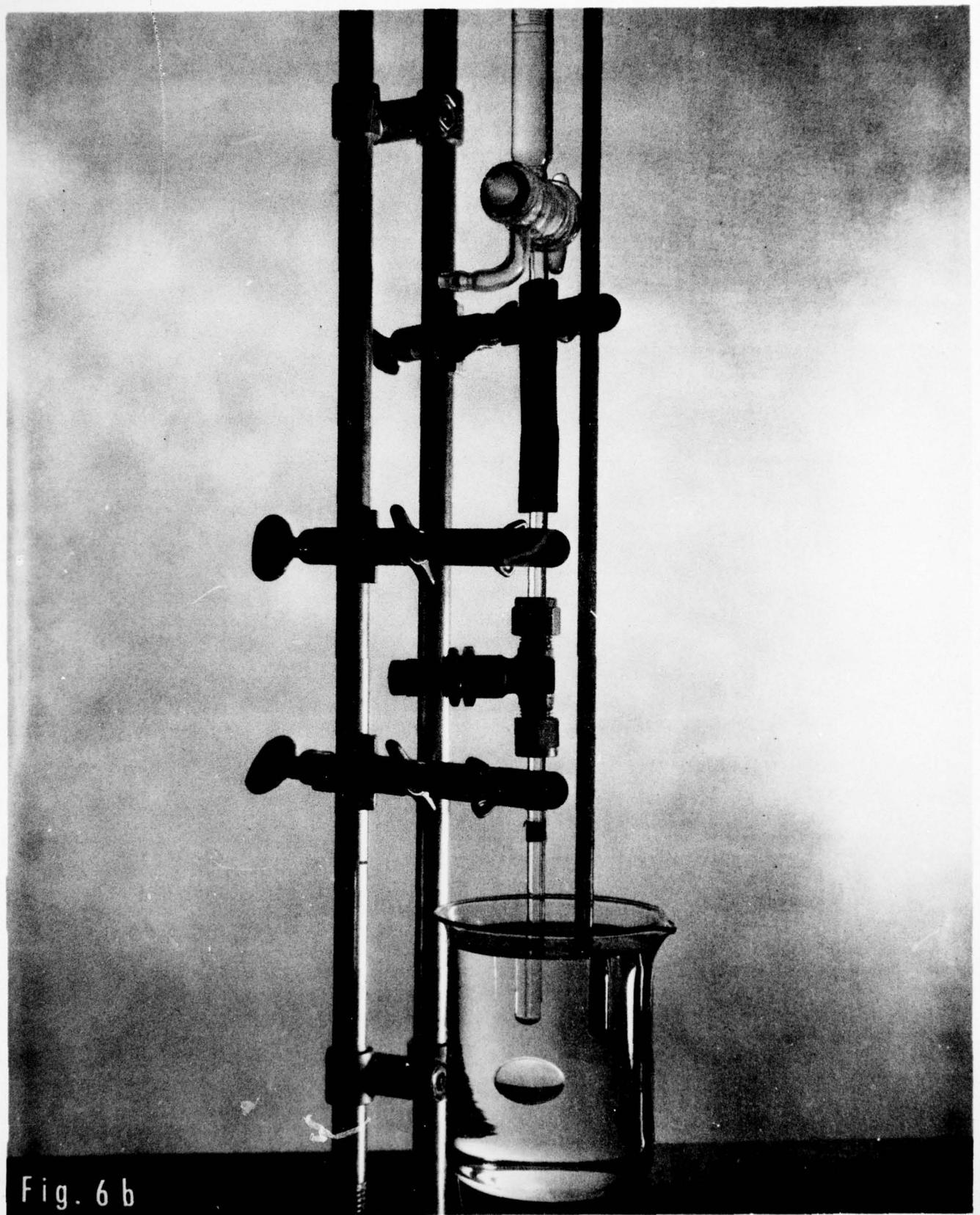


Fig. 6 b

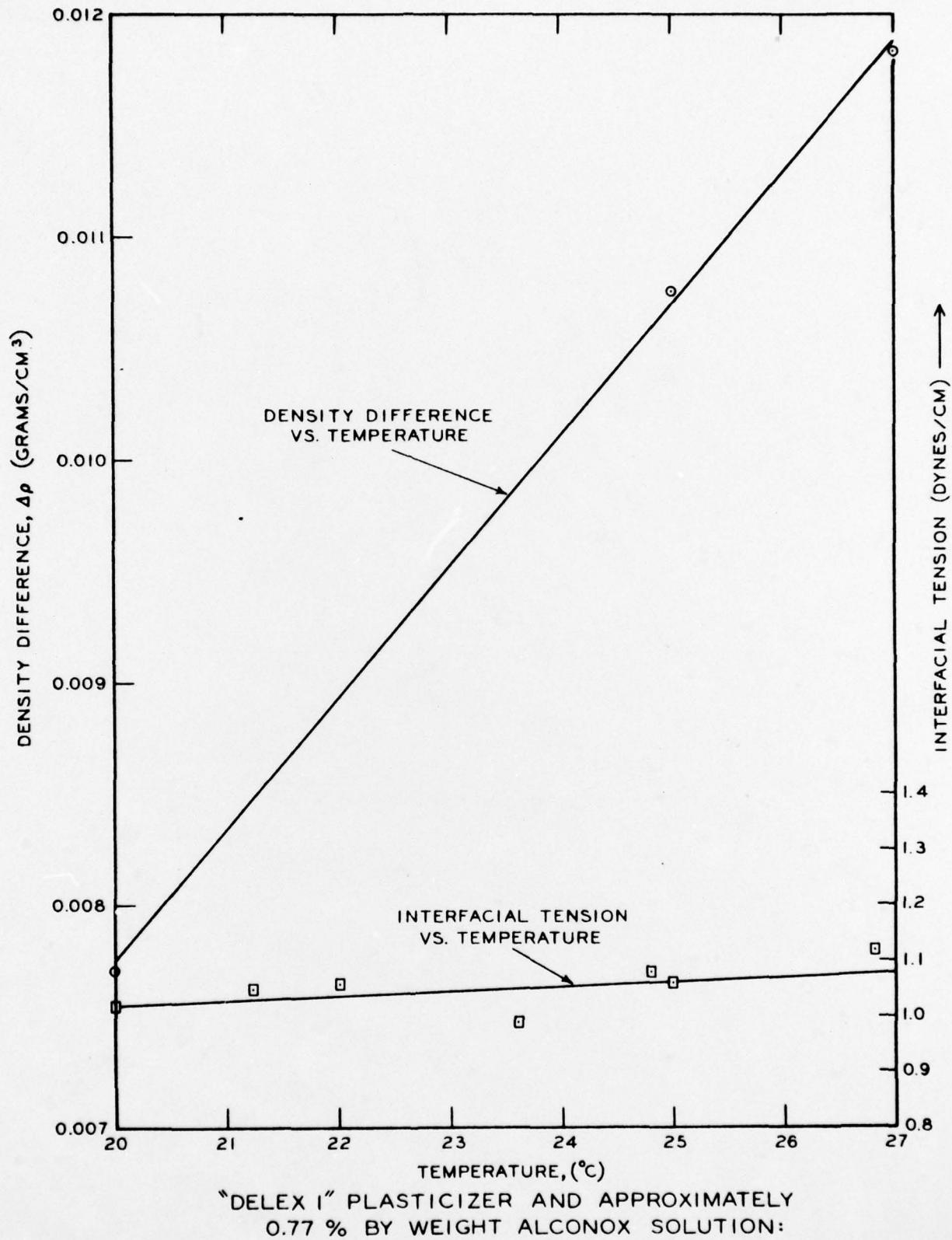


FIG. 7

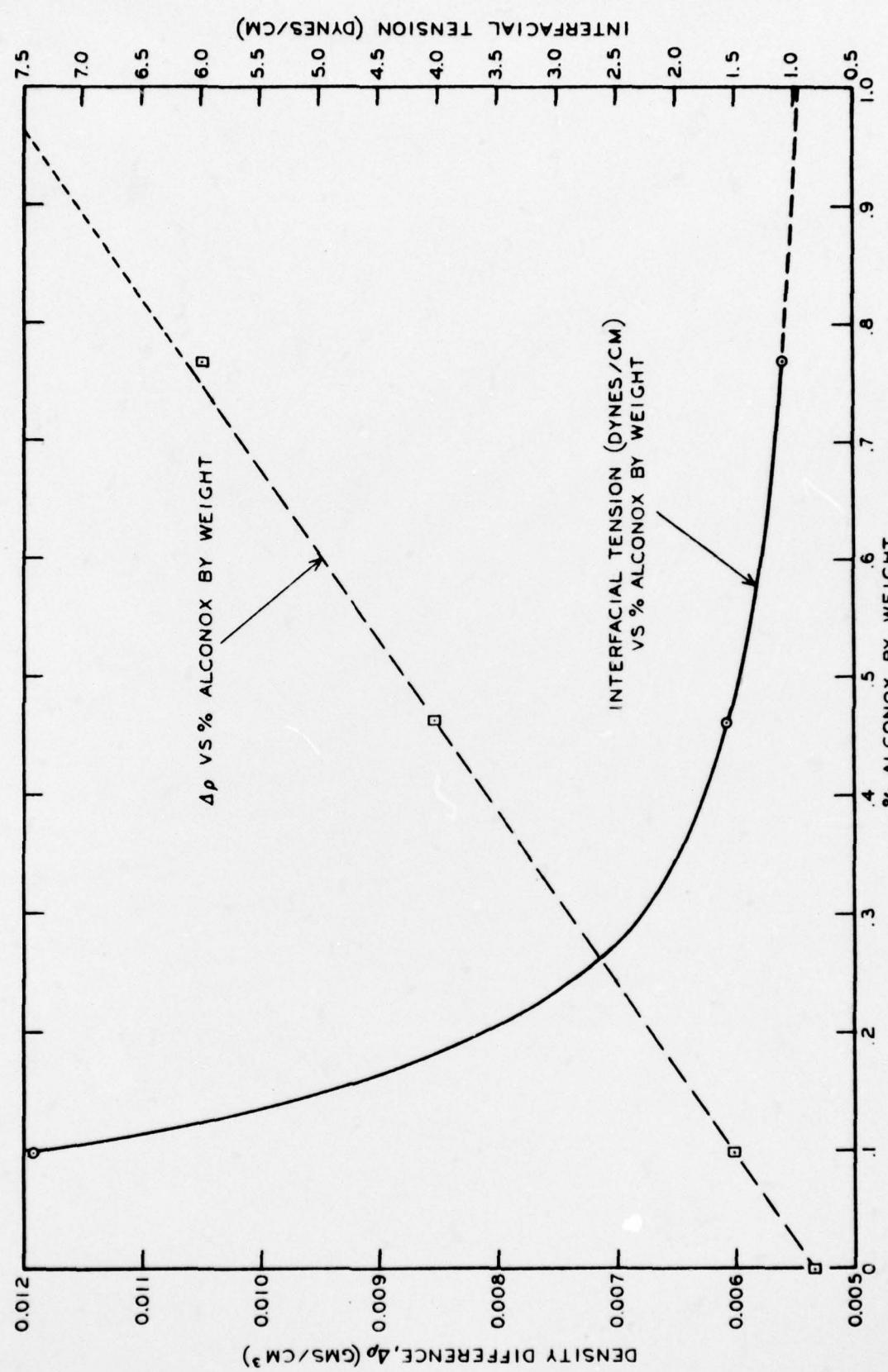


FIG. 8
FOR "DELEX I" PLASTICIZER AND ALCONOX SOLUTIONS AT 25°C

FIG. 8